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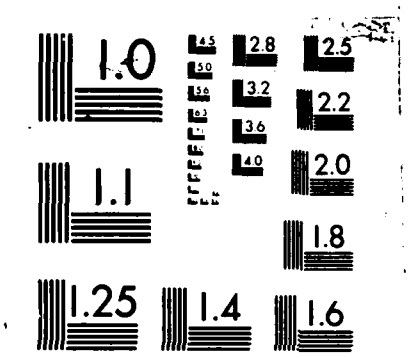

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PBT,PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electrical Conductivity

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This project involves collaborative synthetic, polymer processing, and physicochemical work aimed at exploiting the unique properties of the high modulus/high strength polymers, poly(p-phenylenebenzobisthiazole) (PBT) and poly(p-phenylenebenzobisoxazole) (PBO), for electronic charge transport and nonlinear optical applications. In the former area, we are exploring the properties of macromolecular/macromolecular and molecular/macromolecular hybrid materials constructed from PBT, PBO, and phthalocyanine metallomacrocycles. In the second thrust we are exploring the combination of judiciously selected processing strategies with electro-optic chromophore doping or direct incorporation in the polymer backbone.

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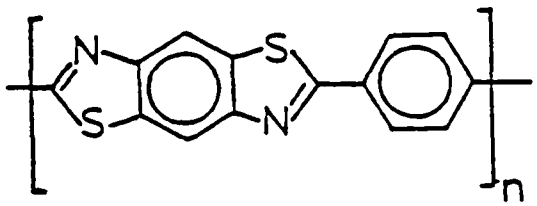
INTRODUCTION

As materials, polymers offer unexcelled diversity and tailorabilty in terms of light weight, strength, elasticity, plasticity, chemical and corrosion resistance, toughness, thermal stability, friction resistance, and processability with regard to forming films, foils, fibers, coatings, etc. Traditionally, however, the application of polymers in optics technology has been limited largely to inexpensive lenses, prisms, fiber optics, anti--reflection coatings, filters, etc. In electronics technology, the attractive properties of polymers have principally been exploited only in insulator fabrication, with little attention being devoted to device applications based on charge transport. It is very clear, however, that in both areas the traditional pictures are rapidly changing, and recent discoveries in the areas of polymeric/organic materials with high electronic conductivity[1,2] or with highly nonlinear optical properties[1,3,4] signal that new generations of advanced materials for optics and electronics technology await synthesis, characterization, and application.

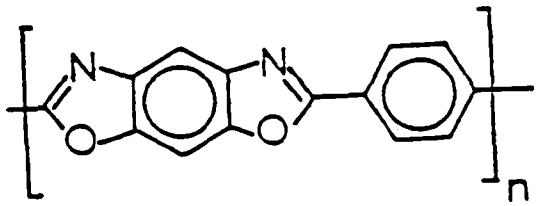
Progress in both of the above areas requires an integrated, multidisci--plinary attack involving synthesis, processing, and physical measurements. In both areas, there is a key, dominant synthetic/architectural requirement of microstructural control to afford the tailored arrays of molecular subunits necessary for facile charge transport or enhanced electronic nonlinear optical polarization response. There is also the requirement that the resulting polymers have superior processing, mechanical, and environmental stability characteristics. In the area of processable conductive polymers, realistic consequences include new types of photoconductive sensors, EMP/EMI materials,

RAS/RAM components, extreme service plastic conductors, electronic device components, and energy cell (battery) components. In terms of technology, realistic consequences of break--throughs in polymeric materials with nonlinear optical properties include new advances in optical telecommunications, optical information processing, and integrated optics.

This project involves collaborative, interdisciplinary effort aimed at developing new types of macromolecular electron-ically conductive and nonlinear optical materials based upon a unique class of polymers developed through the Air Force Materials Laboratory Ordered Polymers Program.[6] These polymers are poly(p-phenylenebenzobisthiazole) (PBT) and poly(p-phenylene--benzo-bisoxazole) (PBO). These robust, rigid-rod macromolecules can be

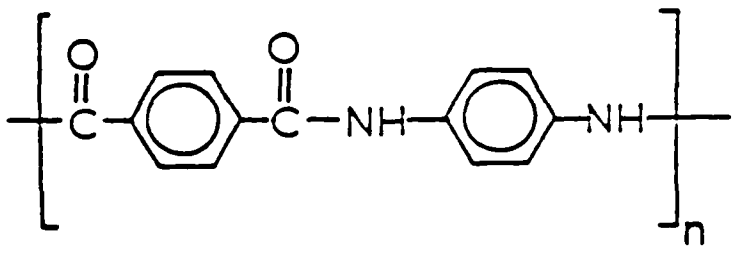


PBT



PBO

processed from acid solution to form very high modulus/high strength fibers and films. For example, proper processing of PBT yields fibers with a modulus over four times that of Kevlar-29. Despite the many attractive properties of



Kevlar

PBT and PBO and the great deal that has been learned about these materials, we suggest that untapped opportunities await exploitation of PBT and PBO in the areas of electrically conductive polymers and nonlinear optical materials. Our objectives with PBT and PBO are:

1. To determine whether strong, flexible, processable, highly conductive macromolecular/macromolecular and molecular/macromolecular hybrids can be produced with phthalocyanine-based electrical conductors.
2. To advance our general understanding of structure/performance relationships in both of the above areas.
3. To determine whether strong, flexible processable highly efficient nonlinear optical materials can be obtained by appropriate "doping" and orientational processing.
4. To determine whether strong, flexible, processable, highly efficient nonlinear optical materials can be obtained by modifying the polymer backbone and orientational processing.
5. To advance our general understanding of structure/performance relationships in both of the above areas.
6. To advance our understanding of how to employ elecrical fields in the processing of stiff chain polymer systems.

PROCESSING STUDIES

A central theme in all PBT,PBO studies described herein is the ability to accurately and reproducibly fabricate macroscopic polymer sturctures with optimized orientational, electrical, mechanical, and optical properties. An in-house capability to process PBT in unusual forms (e.g., containing added "molecular metals," or molecular nonlinear optical chromophores), in unusual solvents, in unusual enviroments (e.g., in a poling field), or with a consid--erably modified backbone architecture, was planned as a major first objective. Extensive collaboration with the Ordered Polymers Group at Wright-Patterson has also been an essential part of this effort.

Progress to Date and Proposed Research

Work accomplished during the first year of AFOSR funding has aimed to: 1) master the handling of PBT in polyphosphoric acid (PPA) or triflic (trifluormethanesulfonic) acid, and 2) bring to full operation a highly-automated, computer-controlled, state-of-the-art fiber wet-spinning apparatus for producing fibers of stiff-chain materials such as PBT, Kevlar, etc. Many of the interrelationships between processing variables and fiber properties have been determined. Manuscripts describing this work are in preparation. The consultation of Marilyn Hunsacker of Wright-Paterson has been invaluable in this connection.

With regard to the handling of PBT in solutions, it was found that satis-factory fibers could be wet-spun from triflic acid but that their mechanical properties were slightly inferior to those spun from PPA. The desirability of triflic acid lies in its unique ability to dissolve many substances which, when co-processed with PBT, will usefully modify the electrical and/or optical characteristics.

Although the mechanical properties of PBT fibers spun to date from triflic acid may be an inherent consequence of using a non-polymeric solvent (such as is the case with PPA), it may alternatively be due to the use of spinning dopes having nonoptimal PBT concentrations. Thus, one aim of work is to carry out a thorough study of the solution physical chemistry of these solutions. We have begun this effort following the approach of Flory and Frost.[7,8] A very significant aspect of this approach will be the ability to establish the molecular weight partitioning between the lyotropic and isotropic phases in our PBT in Kevlar solutions. The reason for this lies in the fact that only the long chains exhibit much self-alignment as the solution passes through the wet-spinning process.

It is expected, then, that these calculations will lead naturally to extensive optical microscopy work. The objectives here will be to observe directly the relative amounts of isotropic and lyotropic phases that develop in PBT solutions with triflic acid. It is to be remembered that chemical degradation will limit how long we can work on these solutions. It is hoped that we can obtain PBT's with different levels of conversion (polydispersity is not controllable; it remains near 1.98). This optical microscopy will also launch a novel line of studies with PBT, viz., the direct observation of the precipitation process. We will model this aspect of our proposed work after that of Strathmann,[9] who published extensively on the coagulation of polymers into reverse osmosis membranes. We expect to find out with this study which processing parameters lead to fully-dense (and therefore having maximal properties) solids as opposed to micro-porous precipitates. We point out, however, that highly novel linear and/or nonlinear optical properties may be

achieved in PBT solids by proper exploitation of coagulation into microporous microstructures.

The other area of proposed processing work relates to proper control of hydrodynamics of the solution in the spinnert and in the jet. Here, we focus on the geometry of the hole through which the pressurized PBT passes. Fortunately we have acquired good connections with the Courtaulds Co. in England. They have fabricated for us dies whose shape changes in instructive ways (see Figure 1) that will allow us to spin fibers with high and low degrees of chain orientation preserved during passage out of the cylinder. Unpublished work done in another laboratory at Northwestern will serve to guide our analysis here.

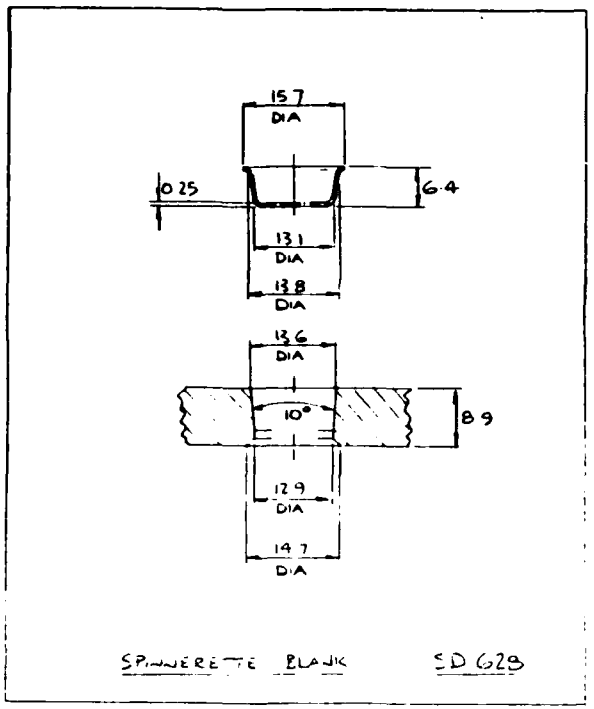
PBT,PBO-BASED ELECTRICALLY CONDUCTIVE POLYMERS

Efforts to synthesize and characterize processable, environmentally stable conductive polymers based upon PBT and PBO have progressed along two lines: 1) doping of pure PBT and 2) preparing molecular/macromolecular hybrid materials based upon PBT and PBO.

Progress to Date and Proposed Research

The chemical structure of the PBT repeat unit suggests an electron-rich π system with a low ionization potential. This property along with a regular, extended architecture is an almost universal prerequisite for an organic electronic conductor.[1,2] Thus, efforts to "dope" (i.e., to bring the electronic structure into a π radical cation state) PBT fibers and films have been initiated. We find that treating as-spun PBT fibers with Br_2 solutions for varying amounts of time results in a dark-red coloration and an increase in electrical conductivity (preliminary room temperature values as high as

a.



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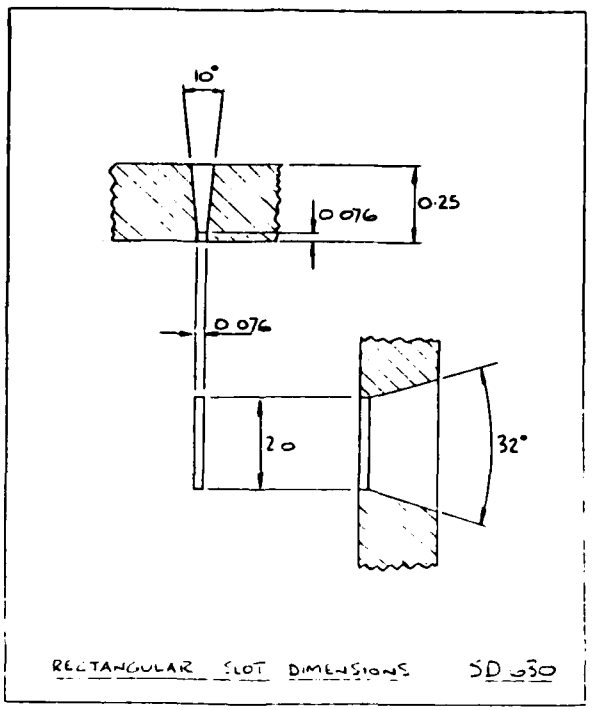

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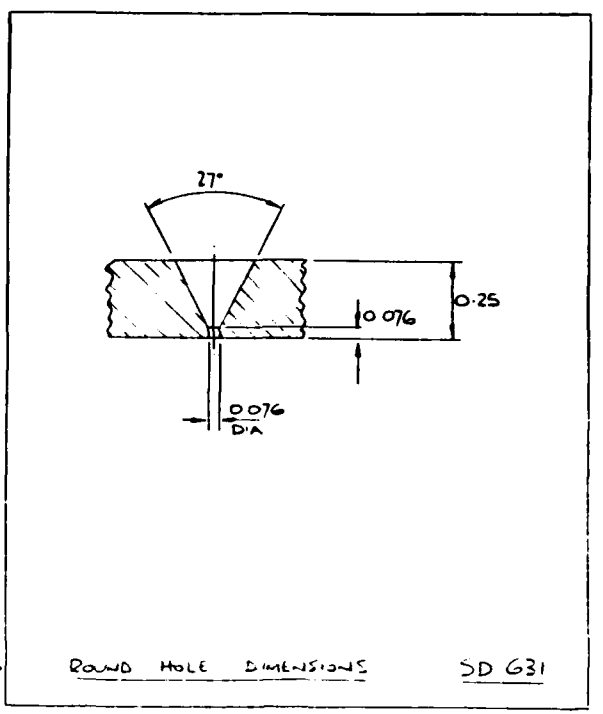

Figure 1. Three drawings of the spinnerettes being used in this study. The upper diagram of 1.a. shows the overall spinnerette geometry. The lower diagram of 1.a. shows the retainer hole for the spinnerette at the bottom of the cylinder. The diagrams in 1.b. and 1.c. show enlarged views of spinnerette holes to be used in the proposed work. The one of 1.b. will make ribbons, and the one of 1.c. will make filaments.

10^{-4} Ω^{-1} cm^{-1} have been measured).[10] The resonance Raman spectrum exhibits a band attributable to Br_5^-, suggesting that oxidation of the polymer backbone has occurred. Studies are now in progress to better define the stoichiometry and structure of the Br_2-doped materials. Addition of Br_2 directly to the spinning dope will also be investigated as a means of more uniformly distributing the dopant. We plan to examine stronger oxidizing agents such as nitrosonium salts (e.g., $NO^+BF_4^-$, $NO^+PF_6^-$)[1d,11] and high-potential quinones (e.g., DDQ, tetrafluoro-TCNQ)[1d,12].

Electrochemical techniques also offer a means to effect p- or n-doping of organic polymers.[2] We have found that flexible, adherent films of PBT can be prepared by dip-coating electrodes with diluted PBT spinning dope. Cyclic voltammetry in THF/$Bu_4N^+BF_4^-$ shows that PBT can be reversibly electrochemically reduced to produce black, conductive films.[13] The reversibility of this process, the amenability to different counterions, and the electrical properties of the resulting films are being investigated. Characterization by optical, magnetic resonance, and diffractometric techniques will follow. In contrast, we find that oxidative electrochemical doping is irreversible.

Another approach to preparing processable, environmentally stable conductive polymeric materials has been to "alloy" molecular conductors (e.g., doped metallophthalocyanine, M(Pc)) or macromolecular conductors (e.g., doped poly(metallophthalocyanines)) with high-modulus aramids having similar solubilities such as Kevlar and Nomex.[1d,14] Preliminary experiments indicate that strong, flexible, environmentally stable, electrically conductive fibers can be spun from solutions of PBT and Ni(Pc) in triflic acid, followed by doping of fibers with iodine solutions.[15] Some representative variable temperature electrical conductivity data are shown in Figure 2. That

significant preferential orientation of the Ni(Pc)I component has taken place during processing is confirmed by polarized resonance Raman experiments (Figure 3). In the Ni(Pc)I crystal structure, I-I-I$^-$ units are arrayed along the crystallographic c axis. The polarization of the totally symmetric I→I→I stretching frequency is thus a measure of the degree of alignment of these oscillators in the conductive fiber.

Studies are now in progress to characterize the structures of the PBT/phthalocyanine hybrid materials and how these depend upon processing methodology by X-ray diffraction, Raman and infrared spectroscopy, high resolution solid state NMR spectroscopy, polarized optical spectroscopy, as well as optical and electron microscopy. Variable temperature four-point conductivity experiments are being used to probe the mechanism and anisotropy of charge transport and how this depends on synthetic (e.g., the identity and quantity of phthalocyanine) and processing procedures. Alternative doping procedures such as bromine oxidation, the use of high-potential quinones and nitrosonium salts, as well as electrochemical oxidation will also be investigated. Although initial efforts will focus on the properties of fibers, efforts to fabricate electrically conductive, PBT-based films will follow. The thermal properties of all new conducting materials are being surveyed by TGA/DSC techniques.

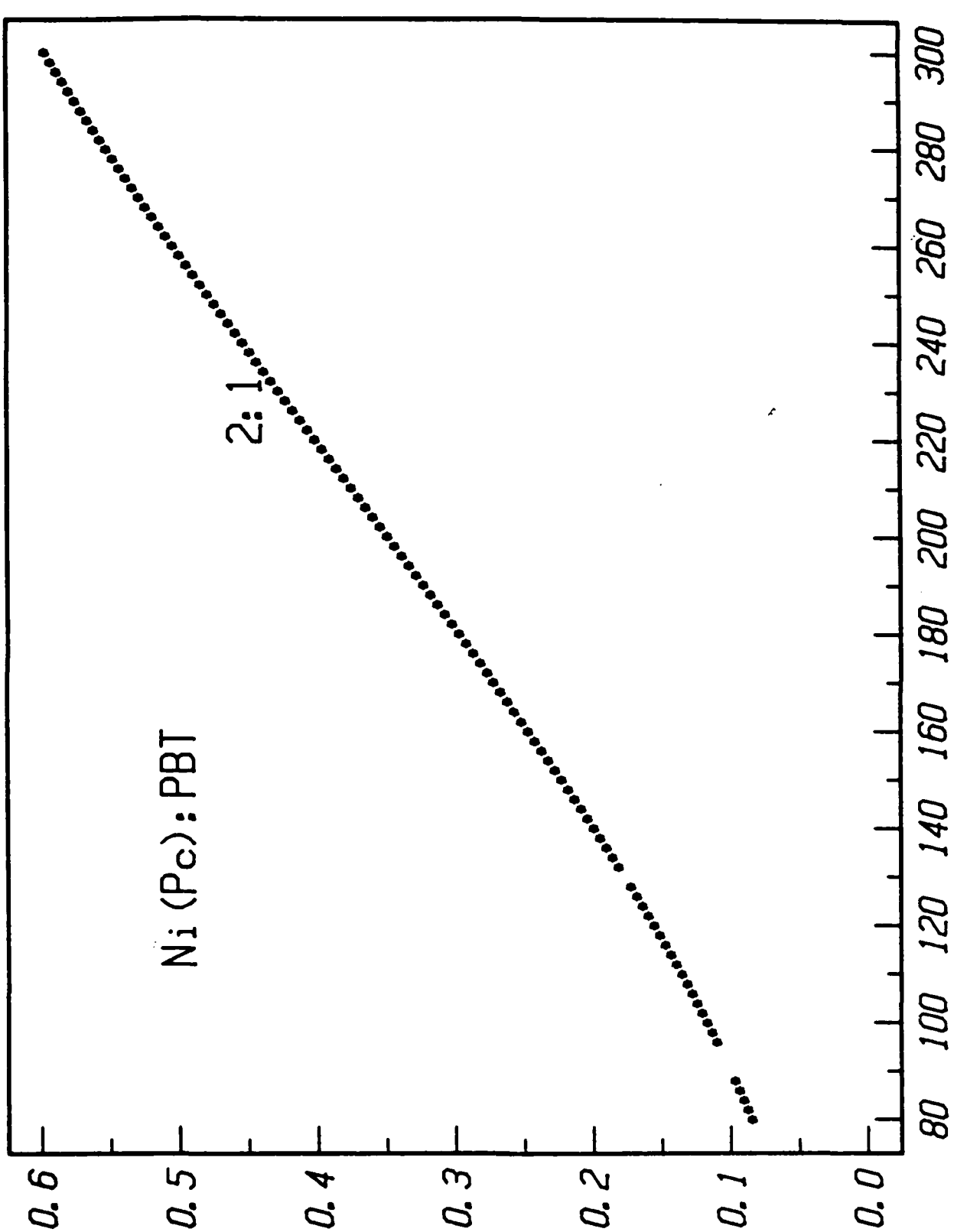

Figure 2. Variable temperature electrical conductivity data for a 2:1 Ni(Pc):PBT fiber doped with iodine.

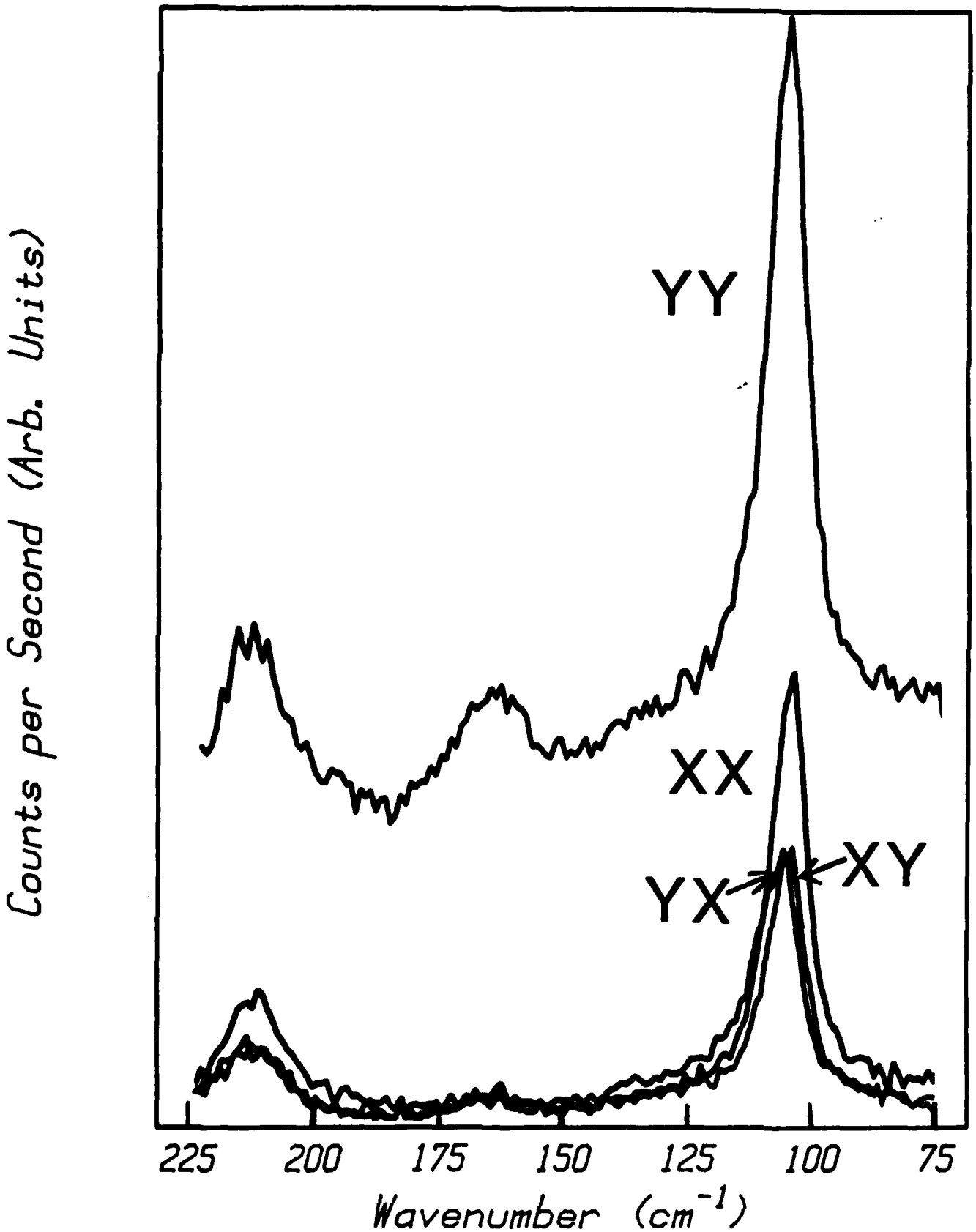

Figure 3. Polarized resonance Raman data for a 2:1 Ni(Pc):PBT fiber doped with iodine. The I_3^- totally symmetric stretching fundamental is observed at 107 cm^{-1}. The Porto polarization symbols give the polarization of the incident and sampled scattered radiation (in the +Z and -Z propagation directions, respectively). The fiber axis is in the Y direction.

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COMPLETED PROJECT SUMMARY

1. PBT,PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electrical Conductivity

2. PRINCIPAL INVESTIGATORS:

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4. CONTRACT/GRANT NUMBER: AFOSR-84-0354

5. COSTS AND FY SOURCE: $150,000

6. SENIOR RESEARCH PERSONNEL:

7. JUNIOR RESEARCH PERSONNEL: P. DePra
J. Giesler
D. Li

8. PUBLICATIONS:

1. Phthalocyanine-Based Electrically Conductive, Processable Molecular/Macromolecular Hybrid Materials, T. Inabe, W.-B. Liang, J. F. Lomax, S. Nakamura, J. W. Lyding, W. J. McCarthy, S. H. Carr, C. R. Kannewurf, and T. J. Marks, Synthetic Metals, 13, 219 (1986).
2. Pi-Electron Calculations for Nonlinear Optical Properties of Molecules, D. Li, T. J. Marks, and Mark A. Ratner, Chem. Phys. Lett., in press.
3. Structure, Charge Transport, and Processing Characteristics of Electrically Conductive Phthalocyanine-Poly(p-phenylenebenzobisthiazole) Hybrid Materials, J. Giesler, P. DePra, H. Marcy, S. H. Carr, C. R. annewurf, and T. J. Marks, manuscript in preparation.
4. Electrochemical Doping of a High-Modulus Rigid-Rod Polymer, J. G. Gaudiello, P. DePra, and T. J. Marks, manuscript in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project involves collaborative synthetic, polymer processing, and physicochemical work aimed at exploiting the unique properties of the high modulus/high strength polymers, poly(p-phenylenebenzobisthiazole) (PBT) and poly(p-phenylenebenzobisoxazole) (PBO), for electronic charge transport and nonlinear optical applications. In the former area, we are exploring the properties of macromolecular/macromolecular and molecular/macromolecular hybrid materials constructed from PBT, PBO, and phthalocyanine metallo-macrocycles. In the second thrust we are exploring the combination of judiciously selected processing strategies with electro-optic chromophore doping or direct incorporation in the polymer backbone.

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